

THE UNHAIRING ACTIVITY OF SODIUM PHOSPHOROTHIOATE

E. H. BITCOVER, H. W. JONES, AND W. WINDUS

*Eastern Utilization Research and Development Division**
Philadelphia, Pennsylvania 19118

INTRODUCTION

It has been proposed that nucleophilic displacement is the key step in the mechanism of unhairing in which the sulfur-sulfur bonds of the cystinyl residues of epidermis and hair are cleaved (1).

Sodium phosphorothioate cleaves the sulfur-sulfur bonds in bovine pancreatic ribonuclease (2) and in cystine (3), and activates papain and ficin (4). The phosphorothioate is considered to be "a potent nucleophilic reagent" (3, 5). It therefore appeared that sodium phosphorothioate might accelerate the unhairing of hides and skins.

EXPERIMENTAL

Sodium phosphorothioate ($\text{Na}_2\text{SPO}_3 \cdot 12\text{H}_2\text{O}$) was prepared by the method of Akerfeldt (6), by reacting sodium hydroxide and phosphorus thiochloride (PSCl_2).

Pieces of brine cured cattle hide (200 grams each) were soaked overnight and washed. One liter of water at room temperature was used to keep the swollen pieces under the liquor in glass jars. Ten percent of hydrated lime was used throughout. Three or six grams of sodium hydroxide was added to the lime controls to duplicate the amount of this alkali that could be formed in the experiments, assuming complete reaction of the sodium phosphorothioate with the calcium hydroxide. Five and ten percent of phosphorothioate on the brine cured weight were used in order to have an adequate amount and to allow for the water of crystallization.

In a separate experiment, 25 percent of sodium phosphorothioate was used with lime to determine whether an excessive amount would damage the hair.

The pieces were stirred several times a day and the hair loosening and slip were tested for three days by the usual "thumb test." The pH of the lime liquors to which five percent or ten percent of the sodium phosphorothioate had been added, based on the hide weight, was uniform at 12.6 to 12.7. That of the lime liquor containing 25 percent of the compound, on the same basis, was 13.0.

In order to eliminate the question of the solubility of calcium phosphorothioate, the same tests were repeated using three percent of sodium hydroxide, based on the hide weight, instead of calcium hydroxide.

*Agricultural Research Service, U. S. Department of Agriculture.

In view of a statement in the literature (3) that the cleavage of cystine is greatest at a pH of 9.5 to 10.0, tests were run at pH's of 8.0, 9.5, and 11.2, the latter being the pH of the phosphorothioate solution. Calcium hydroxide or sodium hydroxide was added after one or three days.

DISCUSSION

In all tests using either calcium or sodium hydroxide, the sodium phosphorothioate accelerated the unhairing moderately. This was particularly evident after one and two days. However, the unhairing activity was not pronounced. The high amount of sodium phosphorothioate produced no change in the appearance of the hair. This is in marked contrast to the action of sodium sulfide alone, and to sodium cyanide or thiols with lime. Hair is dissolved rapidly when three percent of any of these compounds, based on the hide weight, is used.

When the sodium phosphorothioate was used alone at the lower pH's, little or no hair loosening took place after one or three days. The addition of calcium hydroxide then produced the usual moderate acceleration in the rate of unhairing.

Sodium phosphorothioate would therefore not be considered a strong nucleophile by the standards of the leather industry.

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